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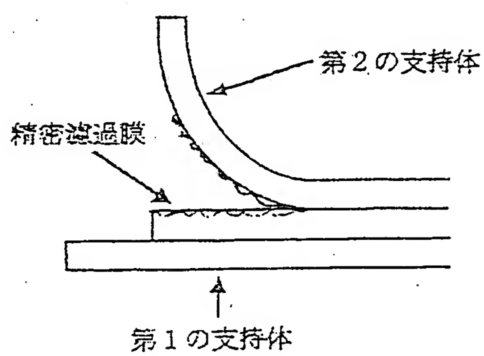
(54) [Title of the Invention] **Microporous membrane and production of same**

(57) [Abstract]

[Problem] To provide a microporous membrane that maintains thickness approximately equal to that of the microfiltration membrane that constitutes its base, while evenly stripping the skin layer on the secondary face, or both skin layers, to produce a highly porous skin layer having a multitude of pores present on said surface, so as to maintain a

high level of filter efficiency of particles, etc. while improving the rate of filtration and extending filter life.

[Solution] A method for production of a microporous membrane [comprising the steps of] stripping the low-porosity skin layer on the secondary face of a microfiltration membrane; applying, by adhesive or thermal means, to each surface of the microporous membrane [i] a microporous membrane having higher porosity than said skin layer and [ii] a sheet support material having a smooth surface devoid of voids and capable of intimate adhesion over its entire face; affixing the sheet support material on the primary face and stripping the sheet support material on the secondary face together with the skin layer of said microfiltration membrane; and neutralizing the adhesive force of said sheet support material on the primary face with a solvent to allow it to be stripped from the said microfiltration membrane without altering the skin phase.



[Key to figure, top to bottom: second sheet support material; microfiltration membrane; first sheet support material]

[Claims]

[Claim 1] A microporous membrane having enhanced porosity of a skin layer by means of stripping the low-porosity skin layer on the secondary face of a microfiltration membrane.

[Claim 2] A microporous membrane having enhanced porosity of both skin layers by means of stripping the relatively high-porosity skin layer on the primary face in addition to the skin layer on the secondary face of a microfiltration membrane.

[Claim 3] A method for production of a microporous membrane according to claim 1, [comprising the steps of] applying, by adhesive or thermal means, to each surface of a microfiltration membrane a sheet support material having a smooth surface devoid of voids and capable of intimate adhesion over its entire face; affixing the sheet support material on the primary face and stripping the sheet support material on the secondary face together with the skin layer of said microfiltration membrane; and neutralizing the adhesive force of said sheet support material on the primary face with a solvent to allow it to be stripped from the said microfiltration membrane without altering the skin phase.

[Claim 4] The method for production of a microporous membrane according to claim 2, [comprising the steps of] applying, by adhesive or thermal means, to each surface of a microfiltration membrane a sheet support material having a smooth surface devoid of voids and capable of intimate adhesion over its entire face; initially affixing one of the sheet supports and stripping the other sheet support material together with the skin layer of said microfiltration membrane; again applying, by adhesive or thermal means, another piece of said sheet support material to the skin; affixing the reapplied sheet support and stripping the other sheet support material together with the skin layer of said the reapplied sheet support material on the primary face with a solvent to allow it to be stripped from the said microfiltration membrane without altering the skin phase.

[Detailed Description of the Invention]

[0001]

[Technological Field of the Invention] The present invention relates to a microfiltration membrane useful in a wide variety of applications, such as in the electronics field for

filtering purified water, or for supernatant filtration or sterilizing filtration of food products or pharmaceuticals.

[0002]

[Prior Art] Typically, microfiltration membranes produced by phase conversion techniques, such as those based on cellulose acetate, polysulfones, or polyether sulfones, have smaller pore size in the skin layer of the microfiltration membrane than in the interior thereof. In many cases, the skin layer has fewer pores, i.e., lower porosity.

[0003] This phenomenon occurs, for example, in the case of wet process phase conversion, in which a solution for forming the membrane is cast onto a glass plate or other support and then dipped in a coagulating bath of water, alcohol, etc. to produce the membrane; during the membrane formation process diffusion and outflow of solvent occurs rapidly at the non-glass side (secondary face) so that nucleation begins to occur, making it difficult to form pores with non-solvents (pore forming agents). Thus, pores forming on the smooth face tend to be small and few in number.

[0004] As a way to increase the number of pores on the surface of a microporous membrane, Unexamined Patent Application 4-4025 proposes a technique in which a thin layer of the skin layer is stripped to expose the inner layer, which has more higher [sic] porosity than the skin layer.

[0005] Examined Patent Publication (Kokoku) 55-6406 proposes a technique in which a microporous sheet whose layer of largest pore size is situated in the interior of the microfiltration membrane is split in two in the thickness direction to remove the layer on the primary face, producing an internal structure in the thickness direction that is a trapezoidal structure wherein pore size becomes progressively smaller across the thickness of the microporous sheet going towards the secondary face.

[0006]

[Problems Which the Invention Attempts to Solve] In most cases, most [sic] microfiltration membranes produced by conventional phase conversion techniques have smaller pores at the surface than in the interior of the membrane, and fewer pores, i.e. lower porosity, in the skin layer. Accordingly, there is a need to reduce resistance to

passage of liquid in the skin layer, and to reduce capture at the surface while increasing capture in the interior in order to improve the rate of filtration and extend filter life.

[0007] While Unexamined Patent Application 4-4025 proposes a technique of removing a thin layer of the skin layer, [the process] tends to remove not only the skin layer but also the internal mesh-like porous layer that captures particulates and the like. Accordingly, there is a need for a method for controlled removal of a thinner layer of material.

[0008] While Examined Patent Publication (Kokoku) 55-6406 proposes a method in which a flat plate is simply adhered to one face of the microfiltration membrane and the microporous membrane then stripped with the flat plate in order to effect splitting thereof within the layer having the largest pore size within the membrane interior. However, as most microfiltration membranes lack strength, there is a significant likelihood of damage to the microporous membrane during stripping. Accordingly, there exists a need for a method by which a microfiltration membrane may be stripped without damaging it. [The publication] further teaches the possibility of using both of the filter membranes obtained by splitting in two as filter products; however, splitting the material into two equal parts requires that the largest pores be situated in the central layer of the base membrane; if this is not the case, one of the [split] membranes must be discarded, resulting in higher production costs. Accordingly, there is a need for improved productivity. Further, since the material is split through the layer having the largest pores in the membrane interior, the surface thereof on the secondary face will have a skin layer with smaller pores than in the membrane interior, and fewer pores, [i.e.] lower porosity. Accordingly, there is need to improve the rate of filtration and extend filter life.

[0009] To solve these problems, the invention provides a microporous membrane endowed with increased porosity of the skin layer on the secondary face by means of evenly stripping the skin layer on the secondary face, without damaging the microfiltration membrane. The invention further provides a microporous membrane having increased porosity on both sides thereof, by means of stripping the skin layer on the primary face of the microporous membrane.

[0010]

[Means Used to Solve the Problems] To achieve these objects the invention provides a microporous membrane having enhanced porosity of a skin layer by means of stripping the low-porosity skin layer on the secondary face of a microfiltration membrane.

[0011] [The invention further provides] a microporous membrane having enhanced porosity of both skin layers by means of stripping the relatively high-porosity skin layer on the primary face in addition to the skin layer on the secondary face of a microfiltration membrane.

[0012] [The invention still further provides] a method for production of a microporous membrane according to claim 1, [comprising the steps of] applying, by adhesive or thermal means, to each surface of a microfiltration membrane a sheet support material having a smooth surface devoid of voids and capable of intimate adhesion over its entire face; affixing the sheet support material on the primary face and stripping the sheet support material on the secondary face together with the skin layer of said microfiltration membrane; and neutralizing the adhesive force of said sheet support material on the primary face with a solvent to allow it to be stripped from the said microfiltration membrane without altering the skin phase.

[0013] [The invention still further provides] a method for production of a microporous membrane according to claim 2, [comprising the steps of] applying, by adhesive or thermal means, to each surface of a microfiltration membrane a sheet support material having a smooth surface devoid of voids and capable of intimate adhesion over its entire face; initially affixing one of the sheet supports and stripping the other sheet support material together with the skin layer of said microfiltration membrane; again applying, by adhesive or thermal means, another piece of said sheet support material to the skin; affixing the reapplied sheet support and stripping the other sheet support material together with the skin layer of said the reapplied sheet support material on the primary face with a solvent to allow it to be stripped from the said microfiltration membrane without altering the skin phase.

[0014] A fuller understanding of the invention is provided through the following description of the production process sequence of the microporous membrane herein.

First, a first surface of the microfiltration membrane is applied by adhesive or thermal means to a first support material having a smooth surface devoid of voids and capable of intimate adhesion over its entire face.

[0015] The material for the first support material is not critical provided that it has a smooth surface devoid of voids and capable of intimate adhesion over its entire face; to facilitate subsequent processing, laminate film composed of plastic sheeting coated with an adhesive is suitable. The plastic sheeting for the laminate film may consist, for example, of polystyrene, polyethylene, polypropylene, polyester, etc.

[0016] Next, a second support of a pliable sheet material that has a smooth surface devoid of voids and capable of intimate adhesion over its entire face is applied by adhesive or thermal means to the other face [of the microfiltration membrane]. The material for the first support material is not critical provided that it has a smooth surface devoid of voids and capable of intimate adhesion over its entire face; to facilitate subsequent processing, laminate film is suitable. The plastic sheeting for the laminate film may consist, for example, of polystyrene, polyethylene, polypropylene, polyester, etc.

[0017] Next, the pliable second support material is peeled away to remove only the skin layer adhering to the second support material, producing a surface having a porous network structure that, seen in plan view, is highly porous with a multitude of pores.

[0018] To peel away the first support material, the material may be wetted with or immersed in a solvent --such as water or alcohol-- that neutralizes the adhesive force of the first support material. Once the adhesive force of the first support material has been neutralized, it is peeled from the microfiltration membrane, affording a microporous membrane having one unaltered face.

[0019] Where laminate film is not used, the adhesive may be any material capable of adhering adequately to the microfiltration membrane, such as polyolefin or polyester based adhesives.

[0020] Where, in addition to the skin layer on the secondary face, one desires to strip the relatively highly porous skin layer on the primary face as well in order to produce higher porosity in both skin layers, the second sheet support material[, once] the first

sheet support material [has been] initially affixed, is stripped together with the skin layer of the microfiltration membrane, and the second sheet support material is [then] re-applied by adhesive or thermal means, this time affixing the second sheet support material while stripping the first sheet support material together with the skin layer of the microfiltration membrane, and then neutralizing with a solvent the adhesive force of the second sheet support material to release it from the microfiltration membrane without altering the skin phase.

[0021]

[Description of the Preferred Embodiments] The invention is described in greater detail through the following Examples and Comparisons.

[0022]

[Comparison 1] A microfiltration membrane was prepared from polyether sulfone using a wet process phase conversion process known in the art. The resultant membrane was an asymmetric microfiltration membrane whose secondary face had a smooth surface containing a small number of small pores; its interior layer [sic][1] became smaller closer to the secondary face; thickness was 120 μm; and filtration efficiency of *Brevundimonas diminuta* was LRV 10.6 or above. An electron microscope image of the secondary face skin phase is shown in Fig. 2.

[0023]

[Comparison 2] A 10 cm square was cut from the microfiltration membrane prepared in Comparison 1, and, using an electric iron, to it was applied a polyester laminate film coated with polyester adhesive, on both sides.[2] The laminate film on the secondary face was then affixed, and the laminate film on the primary face was peeled away to remove the primary face [skin] of the microfiltration membrane together with the laminate film. With the [other] laminate film still adhered to its secondary face, the microfiltration membrane was immersed in a water bath, wetted thoroughly, the laminate film on the secondary face peeled away, and [the membrane] dried to give a microporous membrane.

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[1] [Translator's note: possible omission; "interior layer pore"size?]

[2] [Translator's note: ambiguity in the original reproduced intentionally.]

[0024]

[Example 1] A 10 cm square was cut from the microfiltration membrane prepared in Comparison 1, and, using an electric iron, to it was applied a polyester laminate film coated with polyester adhesive, on both sides. The laminate film on the primary face was then affixed, and the laminate film on the secondary face was peeled away to remove the secondary face [skin] of the microfiltration membrane together with the laminate film. With the [other] laminate film still adhered to its primary face, the microfiltration membrane was immersed in a water bath, wetted thoroughly, the laminate film on the primary face peeled away, and [the membrane] dried to give a microporous membrane An electron microscope image of the surface phase of the skin on the secondary face is shown in Fig. 3.

[0025] Using an electric iron, polyester adhesive-coated polyester laminate film was re-applied to both sides of the microporous membrane prepared in Example 2. The laminate film on the secondary face was then affixed, and the laminate film on the primary face was peeled away to remove the primary face [skin] of the microfiltration membrane together with the laminate film. An electron microscope image of the surface phase of the stripped skin on the primary face is shown in Fig. 5. With the [other] laminate film still adhered to its secondary face (whose porosity had been increased previously), the microfiltration membrane was immersed in a water bath, wetted thoroughly, the laminate film on the secondary face peeled away, and [the membrane] dried to give a microporous membrane having high porosity on both faces.

[0026]

[Performance Evaluations for Comparisons 1, 2 and Examples 1, 2] Sample membranes punched to ϕ47 mm were evaluated for membrane thickness, effectiveness in trapping *Brevundimonas diminuta*, and water filtration rate under partial vacuum (52 cmHg), and samples punched to ϕ25 mm were evaluated for filter life. Results are given in Table 1.

[0027]

[Table 1]

Performance Evaluations for Comparisons 1, 2 and Examples 1,

Sample	Thickness (μm)	Trapping effectiveness	Filtration rate	Filter life (mL)
Comparison 1	88	10.6≤	28.2	728
Comparison 2	87	10.6≤	33.2	1755
Example 1	87	10.6≤	37.9	2089
Example 2	86	10.6≤	38.4	4666

(Note) Target strain for trapping effectiveness: *Brevundimonas diminuta*

Filtration rate: filtration rate of water under partial vacuum (52 cmHg) (mL/cm^2 · min)

Filter life: amount of filtrate [passing through filter] until partial pressure of SNOTEX ZL 100 ppm dispersion reaches 1.5 kg/cm^2

[0028] As indicated in Table 1, the microfiltration membrane of Comparison 2 (primary face stripped) had improved filter life, but negligible improvement in the filtration rate. The microfiltration membrane of Example 1 (having increased porosity on the secondary face) showed both improved filter life and filtration rate. Additionally stripping the skin layer on the primary face of the microfiltration membrane to increase porosity at both faces (Example 2) dramatically improved filter life.

[0029]

[Effects of the Invention] The microporous membrane herein maintains thickness approximately equal to that of the microfiltration membrane that constitutes its base, while evenly stripping the skin layer on the secondary face, or both skin layers, to produce a highly porous skin layer having a multitude of pores present on its surface, so as to maintain a high level of filter efficiency of particles, etc. while improving the rate of filtration and extending filter life. The method for producing the microporous membrane ensures efficiency and economy without damage to the microfiltration membrane per se.

[Brief Description of the Figures]

[Figure 1] A sectional view depicting the stripping process in the invention.

[Figure 2] A 2000x electron microscope image of the surface phase on the secondary face of the microfiltration membrane.

[Figure 3] A 2000x electron microscope image of the secondary face surface phase of the microporous membrane of the invention wherein the secondary face skin layer has been stripped.

[Figure 4] A 2000x electron microscope image of the surface phase on the primary face of the microfiltration membrane.

[Figure 5] A 2000x electron microscope image of the surface phase on the secondary face of the microfiltration membrane of the invention wherein the primary face skin layer has been stripped.

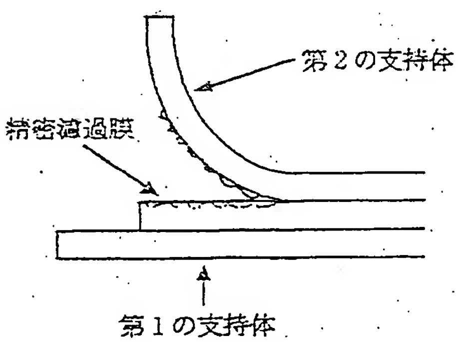
[Key]

1: first sheet support material

2: microfiltration membrane

3: second sheet support material

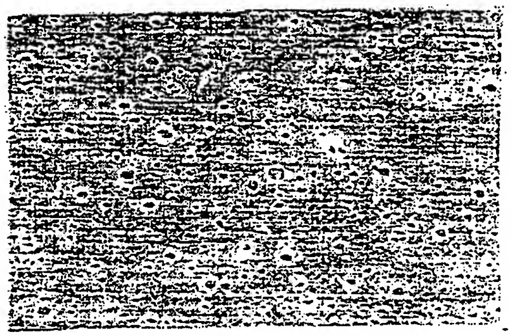
[Fig. 1]



[Key to figure, top to bottom: second sheet support material; microfiltration membrane; first sheet support material]

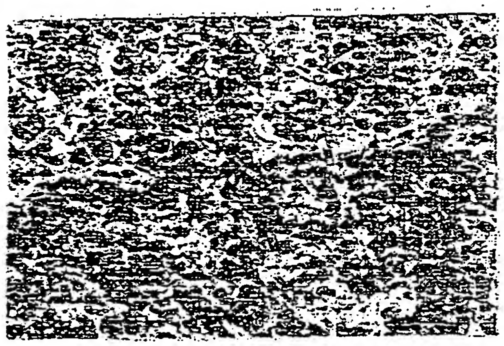
[Fig. 2]

Photograph substituted for drawing



[Fig. 3]

Photograph substituted for drawing



[Fig. 4]

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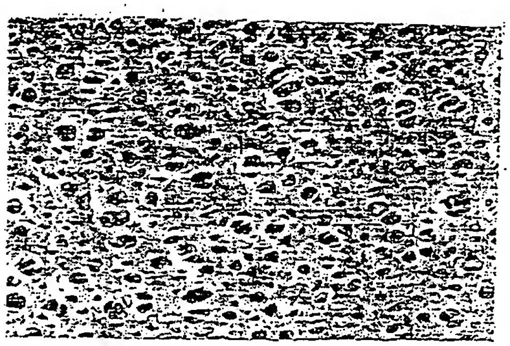

[Fig. 5]

Photograph substituted for drawing